

# Global Phase Behaviour of the Mie Family of Intermolecular Potentials and Its Use in Molecular Modelling of Real Substances

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The Mie ( $m,n$ ) intermolecular potential has been suggested as an alternative to the traditional (12-6) Lennard-Jones potential for modelling real systems both via simulations and theory. Its implementation as a molecular-based equation of state leads to accurate derivative thermophysical properties [1], which cannot be obtained when potentials of fixed repulsive range are considered. An additional advantage is noted in coarse grained models, where as the “superatoms” become larger, the effective potentials are seen to become softer [2] [3]. However, with the exception of a few studies [4] [5], the global (solid-liquid-vapour) phase behaviour of Mie systems is relatively unknown. In this work molecular dynamic simulations are carried out on a number of Mie systems varying in range. The solid, liquid and vapour phases and the transitions are considered and the global phase behaviour is presented quantitatively for these systems. The application of the principle of corresponding states is discussed with the focus of obtaining a unified view of this non-conformal class of fluids. A three-parameter corresponding states model is presented in which a cohesive third parameter,  $\alpha$  is proposed. The  $\alpha$  parameter is an explicit function of the repulsive and attractive exponents and consequently dictates the shape of the intermolecular potential curve. The fluid range, i.e. the ratio between the critical ( $T_c$ ) and triple ( $T_t$ ) points, is obtained from the simulation results and is found to have a linear dependency on  $\alpha$ . The limit where the Mie potential has no stable liquid phase is predicted and the result is in excellent agreement with previous studies [5] [6]. This unique relation between the fluid range and  $\alpha$  can be used to determine molecular models of real systems, coarse graining and united atom forms which lead to consistent ratios of  $T_c$  and  $T_t$  in model systems.

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